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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>5</sup> :</b> <b>C09D 133/06, 127/12, 163/00</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 94/26830</b> <b>(43) International Publication Date:</b> 24 November 1994 (24.11.94)
<b>(21) International Application Number:</b> PCT/US94/04963 <b>(22) International Filing Date:</b> 10 May 1994 (10.05.94) <b>(30) Priority Data:</b> 08/061,984 14 May 1993 (14.05.93) US <b>(71) Applicant:</b> E. I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). <b>(72) Inventors:</b> BARSOTTI, Robert, John; R.D.2, Box 163A, Coles Mill Road, Franklinville, NJ 08322 (US). ANDERSON, Albert, Gordon; 2410 St. Francis Street, Wilmington, DE 19808 (US). <b>(74) Agents:</b> EVANS, Susan, B. et al.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).		<b>(81) Designated States:</b> CA, JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> ANHYDRIDE-EPOXY COATING COMPOSITION MODIFIED WITH A FLUOROPOLYMER  <b>(57) Abstract</b>  An improved coating composition useful for a finish for automobiles and trucks in which the film forming binder contains reactive binder components of about: (a) 25-90 % by weight, based on the weight of binder, of an acrylic anhydride polymer having at least two reactive anhydride groups and comprising polymerized monomer units of (i) an ethylenically unsaturated anhydride or an ethylenically unsaturated dicarboxylic acid which has been converted to an anhydride, and (ii) monomer units selected from the group consisting of alkyl methacrylate, alkyl acrylate and mixtures thereof, wherein the alkyl groups contain 1-12 carbon atoms, said polymer having a weight average molecular weight of about 2,000-50,000; (b) 5-30 % by weight of an oxiranyl component having at least two reactive oxiranyl groups; (c) 1-30 % of a fluorinated polymer derived from at least one monomer having a perfluorocarbon group of at least 4 carbon atoms, and at least one functional group that can react with component (a) and/or component (b); (d) an effective amount of a curing catalyst; wherein components (a), (b) and (c) are separate components; and optional component (e) comprising about 5-30 %, by weight based on the weight of binder, of one or more resins selected from the group consisting of acrylic, polyester and polyester urethane resins that may contain hydroxyl and/or acid functionality.		

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TITLEANHYDRIDE-EPOXY COATING COMPOSITION  
MODIFIED WITH A FLUOROPOLYMERBACKGROUND OF THE INVENTION

5           This invention relates to an anhydride-epoxy coating composition modified with a fluoropolymer for improved durability.

          There are a wide variety of multi-component coating compositions available for finishing automobiles and  
10   trucks. Various coating compositions comprising anhydride and/or epoxy compositions are known. For example, U.S. Patent 4,906,677 discloses a composition comprising an acrylic anhydride polymer, a glycidyl component, and a phosphonium catalyst.

15           Coating compositions containing fluorinated polymers are known. For example, U.S. Patent 4,581,412 discloses a room temperature curing coating composition comprising copolymers of vinylidene fluoride with other functional ethylenically unsaturated monomers, which may  
20   also be fluorinated, wherein the functional groups are selected from carboxyl, hydroxyl and glycidyl.

          There exists a need to improve durability of coating compositions for automobiles and trucks, or parts thereof. An important aspect of durability is  
25   environmental resistance. The present invention offers a high quality finish exhibiting superior environmental resistance. Such a coating composition exhibits excellent adhesion to the substrate to which it is applied, good outdoor weatherability, etch and mar  
30   resistance, and gloss.

SUMMARY OF THE INVENTION

          The invention is a coating composition comprising 20-80% by weight of binder components (a), (b), (c) and (d), and 80-20% by weight of organic liquid solvent,

wherein said binder components comprise, based on the weight of binder:

(a) 25-90% by weight, based on the weight of binder, of an acrylic anhydride polymer having at least two reactive anhydride groups and comprising polymerized monomer units of (i) an ethylenically unsaturated anhydride or an ethylenically unsaturated dicarboxylic acid which has been converted to an anhydride, and (ii) monomer units selected from the group consisting of alkyl methacrylate, alkyl acrylate and mixtures thereof, wherein the alkyl groups contain 1-12 carbon atoms, said polymer having a weight average molecular weight of about 2,000-50,000;

(b) 5-30% by weight of an oxiranyl component having at least two reactive oxiranyl groups;

(c) 1-30% of a fluorinated polymer having at least one perfluorocarbon group of at least 4 carbon atoms, and at least one functional group that can react with component (a) and/or component (b);

(d) an effective amount of a curing catalyst; wherein components (a), (b) and (c) are separate components; and

optional component (e) comprising 5-30%, by weight based on the weight of binder, of one or more resins selected from the group consisting of acrylic, polyester and polyester urethane that may contain hydroxyl and/or acid functionality. The binder components may also comprise about 2 to 25%, preferably 4-12%, by weight of binder, of the half-ester of an acid anhydride.

In preferred embodiments of the present invention, at least one functional group in component (c) is a terminal or pendant group selected from the group consisting of oxiranyl, hydroxyl, carboxyl, isocyanate, and reactive derivatives thereof.

DETAILED DESCRIPTION OF THE INVENTION

The composition of the present invention forms a durable, environmentally resistant coating for a variety of substrates including plastic, metal, glass, silicon, concrete and wood. The composition is especially useful for finishing the exteriors of automobiles and trucks.

The composition can also be pigmented to form a colored finish, although the composition is particularly useful as a clearcoat.

The coating composition has a high solids content and contains about 20-80% by weight of binder and 80-20% by weight of organic liquid solvent. The binder of the composition comprises about 25-90%, preferably 35-65% by weight of binder, of an acrylic anhydride polymer component (a) containing at least two anhydride groups; 5-30%, preferably 10-20% by weight of binder, of an oxiranyl-containing component (b), and about 1-30%, preferably 5-20% of a fluorinated polymer component (c) containing at least one perfluorocarbon group of at least 4 carbon atoms and also containing at least one functional group that can react with the anhydride groups of component (a) and/or the oxiranyl groups of component (b).

The acrylic anhydride polymer contained in the present composition has a weight average molecular weight of about 2,000-50,000 as determined by gel permeation chromatography with polymethyl methacrylate as a standard. Preferably, the anhydride polymer has a weight average molecular weight of 3,000-25,000.

The acrylic anhydride polymer component (a) is formed by polymerizing one or more monomers of alkyl methacrylates, alkyl acrylates, or mixtures thereof, where the alkyl groups have 1-12 carbon atoms, and ethylenically unsaturated anhydrides, or ethylenically unsaturated dicarboxylic acids which are converted to

the acid anhydride during the polymerization.

Optionally, the acrylic anhydride polymer can contain other monomeric components such as styrene, methyl styrene, acrylonitrile, and/or methacrylonitrile monomer units in amounts of about 0.1-50% by weight.

The anhydride polymer of component (a) may be prepared by conventional techniques in which the monomers, solvent, and conventional catalysts such as t-butyl perbenzoate are charged into a polymerization vessel and heated to about 75-200°C for about 0.5-6 hours to form the polymer.

Typical alkyl acrylates and methacrylates that can be used to form the acrylic anhydride polymer of component (a) are methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate, pentyl methacrylate, hexyl methacrylate, octyl methacrylate, decyl methacrylate, lauryl methacrylate, methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, octyl acrylate, nonyl acrylate, decyl acrylate, lauryl acrylate, and the like. Other components that can be used to form the acrylic anhydride polymer are acrylamide, and methacrylamide. Also, the acrylic anhydride polymer can contain about 0.1-5% by weight of copolymeric units of an ethylenically unsaturated acid such as acrylic acid, methacrylic acid, itaconic acid, maleic acid, and the like.

Typically useful ethylenically unsaturated anhydrides are itaconic anhydride, maleic anhydride, isobutenyl succinic anhydride, and the like. It is also possible to impart the anhydride functionality to the acrylic anhydride polymer by using an ethylenically unsaturated dicarboxylic acid which converts to the acid anhydride during the polymerization reaction. Suitable ethylenically unsaturated dicarboxylic acids that can be



used are itaconic acid, maleic acid, isobutenyl succinic acid, and the like.

A preferred anhydride polymer for use as component (a) is the copolymerization product of styrene, butyl methacrylate, butyl acrylate, and itaconic acid, the latter being converted to an anhydride during polymerization. Another preferred anhydride polymer comprises styrene, butyl methacrylate, butyl acrylate, and itaconic anhydride. Still another preferred anhydride polymer comprises butyl acrylate, styrene, maleic anhydride, and butyl methacrylate.

The oxiranyl component (b) contains at least two oxiranyl groups per molecule and can be an oligomer or a polymer. The oxiranyl groups are preferably glycidyl groups. Typical glycidyl components are sorbitol polyglycidyl ether, mannitol polyglycidyl ether, pentaerythritol polyglycidyl ether, glycerol polyglycidyl ether, low molecular weight oxiranyl resins such as epoxy resins of epichlorohydrin and bisphenol A, di- and polyglycidyl esters of acids, polyglycidyl ethers of isocyanurates, such as Denecol EX301<sup>®</sup> from Nagase. Sorbitol polyglycidyl ethers, such as DCE-358<sup>®</sup> from Dixie Chemical Co., and di- and polyglycidyl esters of acids, such as Araldite CY-184<sup>®</sup> from Ciba-Geigy or XUS-71950<sup>®</sup> from Dow Chemical, form high quality finishes. Cycloaliphatic epoxies such as CY-179<sup>®</sup> from Ciba-Geigy may also be used.

Acrylic polymers containing glycidyl methacrylate or glycidyl acrylate can be used, such as random and block polymers of glycidyl methacrylate/butyl methacrylate. The block polymers can be prepared by anionic polymerization or by group transfer polymerization.

The fluorinated polymers useful in the coating compositions of the present invention have number

average molecular weights in the range of about 200 to 20,000, and weight average molecular weights of about 400 to 100,000. The term "polymer" as used herein includes oligomers such as, for example, tetrafluoro-  
5 ethylene oligomers, which have molecular weights within the above range.

A suitable fluorinated polymer is the product of polymerization of one or more ethylenically unsaturated monomers at least one of which contains fluorine. The  
10 polymer has one or more perfluorocarbon groups which contain at least 4 carbon atoms, and at least one functional group that can react with the anhydride polymer component and/or the epoxy resin component of the coating composition. The fluorinated polymer may  
15 contain about 20 to 100% by weight of repeat units derived from fluorinated monomers, the remainder of the polymer being from non-fluorinated ethylenically unsaturated monomers or other non-fluorinated monomers. Preferably the fluorinated polymer contains about 50 to  
20 100% by weight of fluorinated repeat units.

Fluorinated polymers that are unreactive with the anhydride polymer component and/or the epoxy resin component are unsuitable because of a tendency to  
"bloom" to the surface in an unbound state during  
25 coating application or use, and/or incompatibility with other components which cause haziness in the coatings.

In the preparation of the fluorinated polymer, fluorinated monomers may be copolymerized, or suitable non-fluorinated monomers may be copolymerized with  
30 fluorinated monomers, normally by free-radical initiated addition polymerization. Alternatively, as illustrated in Examples 2 and 3 herein, a fluorinated polymer or "prepolymer" may be reacted with a non-fluorinated compound to form a second fluorinated polymer that can  
35 react with at least one of the other major binder



components and has increased compatibility with said components.

Suitable fluorinated monomers used to form the fluorinated polymer include, but are not limited to, those of the formula  $\text{CF}_2=\text{CFX}$

wherein:

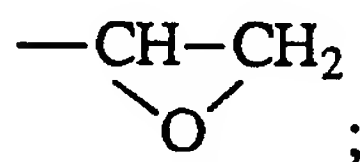
X is -H, -Cl, -F, -R<sub>f</sub>, -OR<sub>f</sub>, -R'<sub>f</sub>-Y or -OR'<sub>f</sub>-Y;

-R<sub>f</sub> is C<sub>1-4</sub> perfluoroalkyl;

-R'<sub>f</sub> is C<sub>1-4</sub> perfluoroalkylene or

-[CF<sub>2</sub>OCF(CF<sub>3</sub>)]<sub>m</sub>[CF<sub>2</sub>]<sub>p</sub>-;

-Y is -OH, -CO<sub>2</sub>H, -CO<sub>2</sub>R, -CN, -CH<sub>2</sub>CH-CH<sub>2</sub>, or



m is an integer of 1-6 and p is an integer of 1-3;

and

R is C<sub>1-6</sub> alkyl, alkali metal, ammonium or quaternary ammonium.

Typical examples of such fluorinated monomers include tetrafluoroethylene, chlorotrifluoroethylene, perfluoropropylene, perfluoroalkylvinyl ethers such as perfluoromethylvinyl ether, perfluorobutylvinyl ether, perfluorocyclohexylvinyl ether, perfluorohydroxybutylvinyl ether, and adducts of such ethers with hexafluoropropene oxide.

Suitable non-fluorinated monomers which may be copolymerized with fluorinated monomers to make the fluoropolymer include, but are not limited to, those of the formula  $\text{CH}_2=\text{CHOZ}$

wherein:

Z is C<sub>1-6</sub> alkyl or -R<sup>1</sup>Y<sup>1</sup>;

R<sup>1</sup> is C<sub>1-6</sub> alkylene;

Y<sup>1</sup> is -OH or -O(CO)R; and

R is defined as above.

Typical examples of such non-fluorinated monomers include alkylvinyl ethers such as methylvinyl ether, butylvinyl ether, cyclohexylvinyl ether, and hydroxybutylvinyl ether.

5 Preferred fluorinated polymers are functional derivatives of so-called "Telomer B" polytetrafluoroethylene oligomers selected from the group consisting of  $F(CF_2)_nCH_2CH-CH_2$ ,  $F(CF_2)_nCH_2CH_2-Y^1$  and

$$\begin{array}{c} \diagup \\ O \\ \diagdown \end{array}$$

$[F(CF_2)_nCH_2CH_2-O(CO)]_qR^2$  wherein:

10  $Y^1$  is defined as above;

$n$  is 4 to about 20;

$q$  is 2 or 3; and

$R^2$  is a di- or trivalent hydrocarbyl group of up to 6 carbon atoms also containing at least one terminal -OH group.

15 Particularly suitable fluorinated polymers are prepared by reacting the glycidyl functional Telomer B derivative,  $F(CF_2)_nCH_2CH-CH_2$ , with an excess of a half-ester reaction product of a monomeric dicarboxylic acid anhydride such as hexahydrophthalic anhydride or succinic anhydride, which may be substituted, for example, with a  $C_{1-8}$  alkyl group, and a monofunctional or polyfunctional alcohol such as methanol or ethylene glycol. The fluorinated half-ester may contain a pendant carboxyl group and/or a hydroxyl group which contribute to crosslinking of the coating composition of the invention.

20 A suitable fluorinated polymer can also be prepared by reacting said glycidyl functional Telomer B derivative with part of the anhydride resin used as a binder component in the invention coating compositions.

30 In addition to binder components (a), (b), (c), and (d), the present composition may optionally include

component (e) comprising about 5 to 30%, preferably 10 to 25%, based on the weight of the binder components, of an acrylic, polyester or polyester urethane polymer, or copolymer thereof which may also contain hydroxyl and/or acid functionality. If said functionality is hydroxyl, the hydroxyl number is about 20 to 120, preferably 70 to 100. If the functionality is acid, the acid number is about 20 to 120, preferably 75 to 95. These polymers have a weight average molecular weight of about 2,000 to 20,000, preferably 4,000-10,000. These polymers contribute to the outdoor weatherability of the coating prepared from this coating composition.

Polyester urethanes are a reaction product of a hydroxyl terminated polyester component and a polyisocyanate component, preferably, an aliphatic or cycloaliphatic diisocyanate. A polyester, which may be used alone or as the polyester component of a polyester urethane, may be suitably prepared from linear or branched chain diols, including ether glycols, or mixtures thereof or mixtures of diols and triols, containing up to and including 8 carbon atoms, or mixtures of such diols, triols, and polycaprolactone polyols, in combination with a dicarboxylic acid, or anhydride thereof, or a mixture of dicarboxylic acids or anhydrides, which acids or anhydrides contain up to and including 12 carbon atoms, wherein at least 75% by weight, based on the weight of dicarboxylic acid, is an aliphatic dicarboxylic acid.

Representative saturated and unsaturated polyols that can be reacted to form a polyester include alkylene glycols such as neopentyl glycol, ethylene glycol, propylene glycol, butane diol, pentane diol, 1,6-hexane diol, 2,2-dimethyl-1,3-dioxolane-4-methanol, 1,4-cyclohexane dimethanol, 2,2-dimethyl 1,3-propanediol, 2,2-bis(hydroxymethyl)propionic acid, and 3-mercapto-

1,2-propane diol. Preferred are 1,6-hexanediol and butylene glycol.

Polyhydric alcohols, having at least three hydroxyl groups, may also be included to introduce branching in the polyester. Typical polyhydric alcohols are tri-  
5 methylol propane, trimethylol ethane, pentaerythritol, glycerin and the like. Trimethylol propane is preferred, in forming a branched polyester.

Polycaprolactone polyols may also be used in making the polyester. A preferred polycaprolactone, a triol,  
10 is Tone® FCP 310 (available from Union Carbide).

The carboxylic acids used in making the polyester component of the polyester urethane include the saturated and unsaturated polycarboxylic acids and the derivatives thereof. Aliphatic dicarboxylic acids used  
15 to form the polyester are as follows: adipic acid, sebacic acid, succinic acid, azelaic acid, dodecanedioic acid, 1,3 or 1,4-cyclohexane dicarboxylic acid and the like. A preferred acid is adipic acid. Aromatic  
20 polycarboxylic acids include phthalic acid, isophthalic acid, terephthalic acid, and the like. Anhydrides may also be used, for example, maleic anhydride, phthalic anhydride, trimellitic anhydride, and the like.

Typical polyisocyanates that may be used to form the polyester urethane are as follows: isophorone  
25 diisocyanate which is 5-isocyanato-1-(isocyanatomethyl)-1,3,3-trimethylcyclohexane, propylene-1,2-diisocyanate, butylene-1,2-diisocyanate, butylene-1,3-diisocyanate, hexamethylene-1,6-diisocyanate, methyl-2,6-diisocyanate  
30 caproate, octamethylene-1,8-diisocyanate, 2,4,4-trimethylhexamethylene-1,6-diisocyanate, nonamethylene diisocyanate, 2,2,4-trimethylhexamethylene-1,6-diisocyanate, decamethylene-1,10-diisocyanate, 2,11-diisocyanato-dodecane and the like, meta-phenylene  
35 diisocyanate, para-phenylene diisocyanate, toluene-2,4-

diisocyanate, toluene-2,6-diisocyanate, xylene-2,4-diisocyanate, xylene-2,6-diisocyanate, dialkyl benzene diisocyanates such as methylpropylbenzene diisocyanate, methylethylbenzene diisocyanate, and the like;

5 2,2'-biphenylene diisocyanate, 3,3'-biphenylene diisocyanate, 4,4'-biphenylene diisocyanate, 3,3'-dimethyl-4,4'-biphenylene diisocyanate, and the like; methylene-bis(4-phenyl isocyanate), ethylene-bis(4-phenyl isocyanate), isopropylidene-bis(4-phenyl isocyanate),

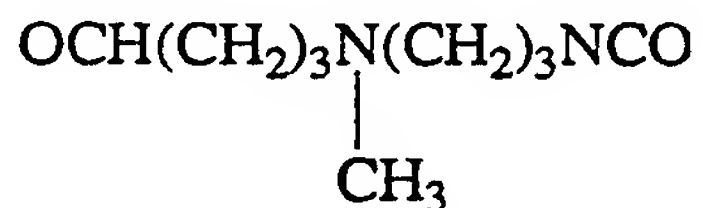
10 butylene-bis(4-phenylisocyanate), and the like; 2,2'-oxydiphenyl diisocyanate, 3,3'-oxydiphenyl diisocyanate, 4,4'-oxydiphenyl diisocyanate, 2,2'-ketodiphenyl diisocyanate, 3,3'-ketodiphenyl diisocyanate, 4,4'-ketodiphenyl diisocyanate, 2,2'-mercaptodiphenyl diisocyanate, 3,3'-mercaptodiphenyl diisocyanate, 4,4'-thiodiphenyl diisocyanate, and the like; 2,2'-diphenylsulfone diisocyanate, 3,3'-diphenylsulfone diisocyanate, 4,4'-diphenylsulfone diisocyanate, and the like;

15 2,2'-methylene-bis(cyclohexyl isocyanate), 3,3'-methylene-bis(cyclohexyl isocyanate), 4,4'-methylene-bis(cyclohexyl isocyanate), 4,4'-ethylene-bis(cyclohexyl isocyanate), 4,4'-propylene-bis-(cyclohexyl isocyanate), bis(para-isocyano-cyclohexyl)sulfide, bis(para-isocyanato-cyclohexyl)sulfone, bis(para-isocyano-cyclohexyl)ether,

20 bis(para-isocyanato-cyclohexyl)diethyl silane, bis(para-isocyanato-cyclohexyl)diphenyl silane, bis(para-isocyanato-cyclohexyl)ethyl phosphine oxide, bis(para-isocyanato-cyclohexyl)phenyl phosphine oxide, bis(para-isocyanato-cyclohexyl)N-phenyl amine, bis(para-isocyanato-cyclohexyl)N-methyl amine, 3,3'-dimethyl-4,4'-diisocyano biphenyl, 3,3'-dimethoxy-biphenylene diisocyanate, 2,4-bis(b-isocyanato-t-butyl)toluene, bis(para-b-isocyanato-t-butyl-phenyl)ether, para-bis(2-

30 methyl-4-isocyanatophenyl)benzene, 3,3-diisocyanato

adamantane, 3,3-diisocyano biadamantane, 3,3-diisocyanatoethyl-1'-biadamantane, 1,2-bis(3-isocyanatopropoxy)ethane, 2,2-dimethyl propylene diisocyanate, 3-methoxy hexamethylene-1,6-diisocyanate, 2,5-dimethyl  
 5 heptamethylene diisocyanate, 5-methyl nonamethylene-1,9-diisocyanate, 1,4-diisocyanato cyclohexane, 1,2-diisocyanato octadecane, 2,5-diisocyanato-1,3,4-oxadiazole,  $\text{OCN}(\text{CH}_2)_3\text{O}(\text{CH}_2)_2\text{O}(\text{CH}_2)_3\text{NCO}$ ,  $\text{OCN}(\text{CH}_2)_3\text{NCO}$  or the following:



10 Aliphatic diisocyanates are preferred, which form urethanes that have excellent weatherability. One aliphatic diisocyanate that is particularly preferred is trimethyl hexamethylene-1,6-diisocyanate.

A preferred polyester urethane is the reaction  
 15 product of trimethylhexamethylene-1,6-diisocyanate and a hydroxy terminated polyester of 1,3-butylene glycol, 1,6-hexanediol, adipic acid, trimethylolpropane, and Tone® FCP 310.

It is noted that a hydroxy functional polyester  
 20 urethane can be converted to the corresponding acid functional polyester urethane by reaction with methylhexahydrophthalic anhydride or other mono-anhydride such as succinic anhydride. Converting the hydroxy to the acid may result in longer pot life in the clearcoat.

25 A polyester may be prepared by conventional techniques in which the component polyols and carboxylic acids and solvent are esterified at about 110-250 °C. for about 1-10 hours to form a polyester. To form a polyester urethane, a diisocyanate may then be added and  
 30 reacted at about 100 °C. for about 15 minutes to 2 hours.



In preparing the polyester urethane, a catalyst is typically used. Conventional catalysts include benzyl trimethyl ammonium hydroxide, tetramethyl ammonium chloride, organic tin compounds, such as dibutyl tin diaurate, dibutyl tin oxide, stannous octoate and the like, titanium complexes, and litharge. About 0.1-5% by weight of catalyst, based on the total weight of the reactants, is typically used.

The stoichiometry of the polyester preparation is controlled by the final hydroxyl number and by the need to obtain a product of low acid number. An acid number below 10 is preferable. The acid number is defined as the number of milligrams of potassium hydroxide needed to neutralize a 1 gram sample of the polyester.

Additional information on the preparation of polyester urethanes is disclosed in commonly assigned U.S. Patent No. 4,810,759, hereby incorporated by reference.

An acid resin is optionally added to the coating composition to give improved color. It does this without adversely affecting the crosslinking between the anhydride and glycidyl components. The acid functional material is formed by polymerizing monomers of alkyl methacrylates, or alkyl acrylates or mixtures thereof, where the alkyl groups have 1-12 carbon atoms, and ethylenically unsaturated acids. Optionally, the acid functional polymer also contains other components such as styrene, methyl styrene, and/or acrylonitrile, methacrylonitrile in amounts of about 0.1-50% by weight.

Typical alkyl acrylates, methacrylates, and other components that can be used to form the acid functional polymer are the same as those listed above with respect to the anhydride polymer.

Typically useful ethylenically unsaturated acids are acrylic acid, methacrylic acid, itaconic acid, maleic acid, and the like.

This acid resin may also contain hydroxyl functionality by using monomers such as hydroxyethylacrylate, hydroxyethyl methacrylate and hydroxypropyl acrylate. The hydroxy functionality may be introduced  
5 by a post reaction of the acid with epoxy containing compounds such as Cardura E<sup>®</sup> from Shell Chemical Company (a glycidyl ester of versatic acid) and propylene oxide.

Another optional component of the present composition is the half ester of an anhydride compound,  
10 as distinguished from a polymer, for example, the reaction product of an acid anhydride such as hexahydrophthalic anhydride or a succinic anhydride, which may be substituted, for example, with a C<sub>1</sub>-C<sub>12</sub> alkyl group, with a monofunctional or polyfunctional  
15 alcoholic solvent such as methanol or ethylene glycol. A preferred half ester is the reaction product of methylhexahydrophthalic anhydride with an alcohol such as ethylene glycol. Other alcoholic solvents are propanol, isobutanol, isopropanol, tertiary butanol, n-butanol,  
20 propylene glycol monomethyl ether, ethylene glycol monobutyl ether, and the like. Such half esters are useful for boosting the solids content of the composition. More particularly, such a half ester is chosen to be a good solvent for the preferred  
25 phosphonium catalyst in admixture with the anhydride component. The half ester is suitably present in the amount of 2 to 25% by weight of binder, preferably 4-12%.

About 0.1-5% by weight, based on the weight of the  
30 binder of the coating composition, of a catalyst is added to enhance curing of the composition. Typical catalysts are as follows: triethylene diamine, quinuclidine, dialkyl alkanol amines such as dimethyl ethanolamine, diethyl ethanol amine, dibutyl ethanol  
35 amine, diethyl hexanol amine and the like, lithium

tertiary butoxide, tri(dimethylaminomethyl)phenol, bis(dimethylamino)propan-2-ol, N,N,N<sup>1</sup>,N<sup>1</sup>-tetramethylethylenediamine, N-methyldiethanolamine, N,N-dimethyl-1,3-propanediamine and 1-dimethylamino-2-propanol or  
5 quaternary ammonium salts such as tert-butyl ammonium bromide, benzyl trimethyl ammonium formate and the like. Preferred catalysts, however, are phosphonium compounds such as are disclosed in U.S. Patent No. 4,906,677, and 1,3-dialkylimidazole-2-thiones such as are disclosed in  
10 U.S. Patent No. 5,084,542; both patents are hereby incorporated by reference in their entirety. Suitable catalysts include benzyltriphenyl phosphonium chloride, tetrabutyl phosphonium chloride, 1-methyl-3-propylimidazole-2-thione and 1-butyl-3-methylimidazole-2-  
15 thione (BTI).

Typical solvents for the coating composition include toluene, xylene, butyl acetate, ethyl benzene, higher boiling aromatic hydrocarbons, amyl acetate, ethyl acetate, propyl acetate, ethylene or propylene  
20 glycol mono alkyl ether acetates.

Generally, the present composition is applied as a coating to a substrate by conventional techniques such as spraying, dipping, draw coating, rolling, or electrostatic spraying.

25 The resulting coating can be dried and cured at temperatures of 100 to 200 °C. Coatings are applied to form a finish typically about 0.5-5 mils thick, and preferably 1-2 mils thick.

To improve weatherability of the clear finish of  
30 the coating composition, about 0.1-5% by weight, based on the weight of the binder, of an ultraviolet light stabilizer or a combination of ultraviolet light stabilizers can be added. These stabilizers include ultraviolet light absorbers, screeners, quenchers and  
35 specific hindered amine light stabilizers. Also, about

0.1-5% by weight, based on the weight of the binder, of an antioxidant can be added.

Typical ultraviolet light stabilizers that are useful are listed in U.S. Patent No. 4,906,677, previously incorporated by reference. Particularly useful ultraviolet light stabilizers that can be used are hindered amines of piperidyl derivatives such as those disclosed in Murayama et al., U.S. Patent 4,061,616, issued December 6, 1977, column 2, line 65, through column 4, line 2, and nickel compounds such as [1-phenyl-3-methyl-4-decanoylpyrazolate(5)]-Ni, bis[phenyldithiocarbamate]-Ni(II), and others listed in the above patent, column 8, line 44 through line 55.

An applicable blend of ultraviolet light stabilizers comprises 2-[2'-hydroxy-3',5'-1(1-1-di-methyl-propyl)phenyl]benzotriazole and bis-[4-(1,2,2,6,6-pentamethylpiperidyl)] 2-butyl-2-[(3,5-t-butyl-4-hydroxyphenyl)methyl] propanedioate. Although the stabilizers can be employed in any ratio, a 1:1 ratio of benzotriazole to propanedioate is preferred.

The composition can be pigmented to form a colored finish or primer. About 0.1-200% by weight, based on the weight of the binder, of conventional pigments can be added using conventional techniques in which a mill base containing pigment, dispersant and solvent is first formed. The mill base is then mixed with the composition to form a colored composition. This composition can be applied and cured as shown above.

The following Illustrative Examples illustrate the preparation of optional components for use in coating compositions according to the present invention.

#### ILLUSTRATIVE EXAMPLE A

This example illustrates, as an optional component for a composition according to the present invention, a polyester urethane solution which is prepared by

charging the following constituents in order into a reaction vessel equipped with a stirrer, a heating source and a reflux condenser:

5	<u>Portion 1</u>	<u>Parts by Weight</u>
	1,3-butylene glycol	173.4
	1,6-hexanediol	163.1
	Trimethylol propane	78.8
	Adipic acid	403.7
10	Toluene	20.0
	<u>Portion 2</u>	
	Propylene glycol monomethyl ether acetate	294.4
	<u>Portion 3</u>	
	Tone® FCP 310	
15	(caprolactone polyol from Union Carbide)	934.9
	Propylene glycol monomethyl ether acetate	185.3
	Hydrocarbon solvent	706.1
	<u>Portion 4</u>	
	Trimethylhexamethylene diisocyanate	290.3
20	Dibutyl tin dilaurate	0.5
	<u>Portion 5</u>	
	Hydrocarbon solvent	<u>69.8</u>
	Total	3320.3

Portion 1 is charged in order into the reaction vessel, and the constituents of Portion 1 are heated to distill water at 140-230 °C. The distillation is continued until the acid number is 6.5 to 8.5. The product is thinned and cooled to 98 to 102 °C. by charging Portion 2 into the vessel. While the constituents in the vessel are maintained at the above temperature, Portion 3 is charged to the reactor in order. Portion 4 is added to the composition at a uniform rate over a 30 minute period while the batch

temperature is maintained at 98-102 °C. A sample is removed and tested for unreacted isocyanate NCO by infrared analysis. The composition is held at the above temperature until there is no unreacted isocyanate in the composition. Portion 5 then is added as a rinse and the resulting composition is allowed to cool to ambient temperatures.

Following this procedure, the resulting composition has a polymer weight solids content of about 61.0%. The polyester urethane has a Gardner-Holdt viscosity of L. The  $M_n$  (number average molecular weight) is 3734.0 and the  $M_w$  (weight average molecular weight) is 7818.0 (by gel permeation chromatography using polystyrene as the standard). The acid content is determined to be 4.9 Meq/g. The hydroxy number is 92.

#### ILLUSTRATIVE EXAMPLE B

This example illustrates, as another optional component for use in the present composition, an acid polymer, more specifically a methacrylic acid resin, which is prepared by charging the following constituents into a reactor equipped with a thermometer, stirrer, dropping funnel, and condenser:

<u>Portion 1</u>	<u>Parts by Weight</u>
Propylene glycol monomethyl ether acetate	155.3
Xylene	103.5
<u>Portion 2</u>	
Butyl methacrylate	174.8
Methacrylic acid	97.1
Butyl acrylate	140.8
Styrene	72.8



Portion 3

	Tertiary butyl peroxy acetate	35.0
	Propylene glycol monomethyl ether acetate	41.7
	Xylene	<u>27.8</u>
5	Total	849.0

Portion 1 is charged into the reactor and heated to its reflux (approximately 140 °C). Portion 2 is premixed and added to the reactor dropwise over a 240 minute period. Portion 3 is premixed and added to the reactor over a 270 minute period concurrent with Portion 3. After the addition is complete, the reactor is held at reflux and then cooled and emptied.

The resulting acid polymer composition has composition of 15% styrene, 36% butyl methacrylate, 29% n-butyl acrylate, and 20% methacrylic acid. The solids content is 60% and the polymer has a Gardner-Holdt viscosity of Z-1. The polymer has a weight average molecular weight of 5000.

The following Examples illustrate the invention. All parts and percentages are on a weight basis unless otherwise indicated.

EXAMPLE 1

A. A Styrene/butyl methacrylate/butyl acrylate/itaconic acid (anhydride) copolymer in the weight ratio of 15/20/38/27 was prepared as follows. A reactor was loaded with 224.3 parts of xylene and heated to reflux temperature of 284 °F (Part I). The following Part II was mixed, the itaconic acid added last, and then fed to the reactor simultaneously with Part III, but starting 5 minutes after the start of Part III, over a period of five hours while maintaining reflux.

<u>Part II</u>		<u>Parts by Weight</u>
	Styrene monomer	87.8
	Butyl methacrylate monomer	117.0
	Butyl acrylate	222.3
5	Xylene	7.2
	Itaconic acid	183.1
<u>Part III</u>		<u>Parts by Weight</u>
	Xylene	42.9
10	Propylene glycol monomethyl ether acetate	29.2

During the polymerization, water was formed by dehydration of the polymerized itaconic acid so the anhydride was formed. This water was continuously removed by a water separator distillation apparatus until a total of 11.8 parts of water per 100 parts of itaconic acid were separated from the distillate. When the required amount of water had been stripped off, the reactor was cooled to 190-210 °F and vacuum applied to remove xylene. Finally, 163.9 parts of propylene glycol monomethyl ether acetate were added under nitrogen.

This polymer solution had a Gardner-Holdt viscosity of Y to Z-2 and a measured solids of 65.0%. The anhydride content was determined to be 2.0 Meq/g and the acid content to be 0.7 Meq/g. The molecular weight was measured by gel permeation chromatography to be  $M_n = 1800$  and  $M_w = 4200$ .

B. A coating composition was prepared by thoroughly blending the following:

<u>Component</u>	<u>Parts by Weight</u>
Anhydride polymer from Part A	47.12
Epoxy 10030*	27.62
Butyl acetate	15.46
5 Catalyst solution**	<u>9.80</u>
<hr/> Total	
	100.00 <hr/>

\*A 1:1 mixture of Denecol® EX622, a sorbitol polyglycidyl ether (from Nagase), and a 60/40 butyl methacrylate/glycidyl methacrylate copolymer from DuPont.

10 \*\*28% 1-butyl-3-methylimidazole-2-thione (BTI) in butyl acetate.

A few crystals of Nile red were dissolved in the coating solution to give a clear solution. The solution was coated onto glass plates to a film thickness of 1 mil (3 plates) or 8 mils (2 plates; controls). The  
15 plates were air-dried overnight at room temperature.

A second coating solution was prepared by adding to 100 parts of the above solution 10.00 parts of Zonyl™TE, a mixture of glycidyl-terminated TFE oligomers supplied by DuPont. A clear solution was obtained after  
20 filtration through a 0.2 micron Millipore® filter. Eight mil coatings of this solution were applied to the three plates previously sub-coated to 1 mil thickness, and air-dried for 48 hours. One of these plates, together with one control plate, were baked at 121 °C.  
25 for one hour and then placed in soapy water. The control turned from red to blue, indicating water penetration through the top layer and into the lower layer. The coating containing the fluorinated polymer showed no color change, indicating no water penetration.

30 In other, similar experiments, coatings prepared as above containing Zonyl™TE that were baked showed no penetration after soaking in aqueous detergent for three days; those that were air-dried but not baked showed slight penetration, while control coatings containing no  
35 Zonyl™TE were extensively penetrated and swollen.

EXAMPLE 2

Coating solutions with and without (control) epoxy-functional fluorinated polymer were prepared as described in Example 1, with the following exceptions.

5 A distillate fraction of Zonyl<sup>TM</sup>TE, boiling at about 175 °C., was used instead of the whole oligomer mixture, and the fluoropolymer solution was prepared by mixing and reacting the Zonyl<sup>TM</sup>TE fraction with anhydride resin and catalyst solution for one hour before the Epoxy  
10 10030 and butyl acetate solvent were added. The solution containing the fluoropolymer and the control solution were both clear. Coatings from both solutions cast on to un-precoated plates and dried in air or nitrogen were also clear, confirming that a  
15 compatiblizing reaction between the Zonyl<sup>TM</sup>TE and anhydride resin had occurred. The fluoropolymer modified coating was far more resistant to water penetration than was the control coating.

In subsequent experiments it was found that  
20 completely clear coatings could be obtained from similar solutions containing unfractionated Zonyl<sup>TM</sup>TE, provided the oligomers were allowed to contact the anhydride resin component of the solution in the presence of BTI catalyst solution for 10 min at 80 °C. prior to adding  
25 the epoxy resin and solvent.

EXAMPLE 3

A. A non-polymeric half-ester was prepared by reacting methylhexahydrophthalic anhydride (MHHPA) and ethylene glycol in a molar ratio of about 2:1 as follows. To a  
30 solution of 2 moles of MHHPA in xylene was added 1 mole of ethylene glycol and the combined solution was heated at 250 °F. for five hours, then cooled to 150 °F. Methanol (0.16 mole) was added, and heating was continued for one hour at 150 °F. About 2% of solvent,  
35 based on total weight, was removed by distillation.

B. A fluorinated half-ester was prepared from the product of Part A as follows: 81.11 parts of the half-ester prepared in Part A, 11.11 parts of propylene glycol monomethyl ether acetate, and 7.78 parts of Zonyl<sup>TM</sup>TE (as described in Example 1) were mixed. The mixture was heated and reacted at 180 °F. for two hours, followed by aging at 120 °F. for one week.

10 C. A clearcoat coating composition according to the present invention was prepared by separately premixing Parts I and II shown below, then thoroughly blending Parts I and II; Part I was mildly heated to dissolve the phosphonium chloride catalyst:

15	<u>Component</u>	<u>Parts by weight</u>
	<u>Part I</u>	
	Itaconic anhydride copolymer (as described in Example 1, Part A)	41.17
20	Propylene glycol monomethyl ether acetate	9.76
	Fluorinated half-ester (from Part B)	7.39
	Xylene	2.86
	Benzyl triphenyl phosphonium chloride	0.69
25	<u>Part II</u>	
	Butyl acetate	3.80
	Silica dispersion:	
	Aerosil <sup>®</sup> R-972 (from Degussa)	1.07
	XU-71950 Diglycidyl ester (from Dow)	4.13
30	Propylene glycol monomethyl ether acetate	5.53
	XU-71950 Diglycidyl ester (from Dow)	14.02
	Methacrylic acid resin (from Illust.Exple B)	6.79

	DISLON® 1984	
	(50%; acrylic flow additive in xylene)	0.23
	TINUVIN® 1130 (UV Screener)	1.54
	TINUVIN® 292 (HALS)	<u>1.02</u>
5	TOTAL	100.00

In the above list, the TINUVIN® hindered amine light stabilizer (HALS) and UV Screener were commercial products from Ciba-Geigy. The DISLON® flow additive was supplied by King Industries. The silica dispersion was prepared by grinding the three listed ingredients together in a sand mill.

The coating, which was applied by spraying the above blend, exhibited excellent resistance to liquid water and humidity, chemical resistance especially under alkaline conditions, mechanical durability (mar resistance) and other film properties.

#### EXAMPLE 4

A clearcoat coating composition according to the present invention was prepared by separately premixing Parts I and II shown below, then thoroughly blending Parts I and II:

	<u>Component</u>	<u>Parts by weight</u>
25	<u>Part I</u>	
	Itaconic anhydride copolymer	37.46
	(as described in Ex 1, Part A)	
	RESIFLOW® S	
	(Acrylic flow additive from Estron Chemical)	0.22
30	Propylene glycol monomethyl ether acetate	13.43
	Catalyst solution*	13.17



Part II

	Butyl acetate	6.54
	ARALDITE® CY184 (Diglycidyl ester from Ciba-Geigy)	18.31
5	LUMIFLON® 916 (Hydroxylated fluoropolymer from Kaneka)	8.25
	TINUVIN® 1130 (UV Screener)	1.56
	TINUVIN® 292 (HALS)	<u>1.06</u>
	<b>TOTAL</b>	<b>100.00</b>

- 10 \*In the above list, catalyst solution refers to a solution containing 62.8% MHHPA-ethylene glycol half-ester (prepared as in Part A of Example 3), 29.9% xylene, and 7.3% of benzyl triphenyl phosphonium chloride; the catalyst components were dissolved by heating to 50-60 °C.

15

The TINUVIN® products were as described in Example 3.

- 20 The coating, which was applied by spraying the above blend, exhibited excellent resistance to liquid water and humidity, chemical resistance under both acidic and alkaline conditions, durability and other film properties.

## WHAT IS CLAIMED IS:

1. A coating composition comprising 20-80% by weight of binder components (a), (b), (c) and (d), and 80-20% by weight of organic liquid solvent, wherein said  
5 binder components comprise, based on the weight of binder:

(a) 25-90% by weight, based on the weight of binder, of an acrylic anhydride polymer having at least two reactive anhydride groups and comprising polymerized  
10 monomer units of (i) an ethylenically unsaturated anhydride or an ethylenically unsaturated dicarboxylic acid which has been converted to an anhydride, and (ii) monomer units selected from the group consisting of alkyl methacrylate, alkyl acrylate and mixtures thereof,  
15 wherein the alkyl groups contain 1-12 carbon atoms, said polymer having a weight average molecular weight of about 2,000-50,000;

(b) 5-30% by weight of an oxiranyl component having at least two reactive oxiranyl groups;

20 (c) 1-30% of a fluorinated polymer derived from at least one monomer having a perfluorocarbon group of at least 4 carbon atoms, and at least one functional group that can react with component (a) and/or component (b);

25 (d) an effective amount of a curing catalyst; wherein components (a), (b) and (c) are separate components; and

optional component (e) comprising about 5-30%, by weight based on the weight of binder, of one or more  
30 resins selected from the group consisting of acrylic, polyester and polyester urethane resins that may contain hydroxyl and/or acid functionality.

2. A coating composition comprising 20-80% by weight of binder components (a), (b), (c) and (d), and  
35 80-20% by weight of organic liquid solvent, wherein said

binder components comprise, based on the weight of binder:

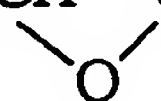
- (a) 25-90% by weight, based on the weight of binder, of an acrylic anhydride polymer having at least two reactive anhydride groups and comprising polymerized monomer units of (i) an ethylenically unsaturated anhydride or an ethylenically unsaturated dicarboxylic acid which has been converted to an anhydride, and (ii) monomer units selected from the group consisting of alkyl methacrylate, alkyl acrylate and mixtures thereof, wherein the alkyl groups contain 1-12 carbon atoms, said polymer having a weight average molecular weight of about 2,000-50,000;
- (b) 5-30% by weight of an oxiranyl component having at least two reactive oxiranyl groups;
- (c) 1-30% of a fluorinated polymer derived from at least one monomer having a perfluorocarbon group of at least 4 carbon atoms, and at least one functional group that can react with component (a) and/or component (b); and
- (d) an effective amount of a curing catalyst; wherein components (a), (b) and (c) are separate components.

3. The coating composition according to Claim 2 wherein the oxiranyl component (b) is selected from the group consisting of a polyglycidyl ether of a polyol, an epoxy resin of epichlorohydrin and bisphenol-A, a polyglycidyl ester of a polycarboxylic acid, a polyglycidyl ether of an isocyanurate, a glycidyl methacrylate or glycidyl acrylate-containing acrylic polymer, and compatible mixtures of any of the above.

4. The coating composition according to Claim 2 wherein the fluorinated polymer component (c) contains at least one functional group which may be terminal or pendant, selected from the group consisting of oxiranyl,

hydroxyl, carboxyl, isocyanate, and reactive derivatives thereof.

5. The coating composition according to Claim 4 wherein the fluorinated polymer is a functional  
 5 polytetrafluoro-ethylene oligomer selected from the group consisting of  $F(CF_2)_nCH_2CH-CH_2$ ,  $F(CF_2)_nCH_2CH_2-Y^1$



and  $[F(CF_2)_nCH_2CH_2-O(CO)]_qR^2$

wherein:

10  $Y^1$  is -OH or -O(CO)R;  
 $n$  is 4 to about 20;  
 $q$  is 2 or 3; and  
 $R^2$  is a di- or trivalent hydrocarbyl group of up to 6 carbon atoms also containing at least one terminal -OH group.

15 6. The coating composition according to Claim 1 wherein component (e) is a polyester urethane having a hydroxyl number of about 20-120 or an acid number of about 20-120.

20 7. The coating composition according to Claim 2 wherein the acrylic anhydride polymer component (a) comprises polymerized monomers of styrene, alkyl methacrylate or an alkyl acrylate having 2-4 carbon atoms in the alkyl group, and an ethylenically unsaturated anhydride or ethylenically unsaturated  
 25 dicarboxylic acid converted to anhydride.

8. The coating composition according to Claim 2 wherein the acrylic anhydride polymer component (a) comprises polymerized monomers of butyl acrylate, styrene and itaconic acid converted to anhydride.

30 9. The coating composition according to Claim 2 wherein the acrylic anhydride polymer component (a) comprises polymerized units of maleic anhydride.

10. The coating composition according to Claim 1 wherein component (e) is an acrylic resin formed by polymerizing monomers selected from ethylenically unsaturated acids, alkyl acrylates and methacrylates, hydroxyalkyl acrylates and methacrylates, and mixtures thereof, where the alkyl groups contain 1-12 carbon atoms.

11. The coating composition according to Claim 2 wherein the catalyst is a phosphonium compound or a 1,3-dialkyl-imidazole-2-thione.

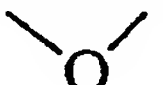
12. The coating composition according to Claim 1 wherein the binder components further comprise about 2-25%, by weight of binder, of a half-ester which is the reaction product of a monomeric anhydride of a dicarboxylic acid and a mono- or polyhydric alcohol.

13. The coating composition according to Claim 12 wherein the binder components comprise 4-12%, by weight of binder, of the half-ester.

14. The coating composition according to Claim 12 wherein the half-ester is the reaction product of a mono- or dihydric alcohol and methylhexahydrophthalic anhydride.

15. The coating composition according to Claim 14 wherein the half-ester is the reaction product of at least about 2 moles of methylhexahydrophthalic anhydride and about one mole of ethylene glycol.

16. The coating composition according to Claim 4 wherein the fluorinated polymer is the product of reaction of one or more glycidyl-functional

polytetrafluoroethylene oligomers,  $F(CF_2)_nCH_2CH-CH_2$ ,  


wherein n is 4 to about 20, and the half-ester of Claim 12, 14 or 15.

17. The coating composition according to Claim 4 wherein the fluorinated polymer is the product of reaction of one or more glycidyl-functional

polytetrafluoroethylene oligomers,  $\text{F}(\text{CF}_2)_n\text{CH}_2\text{CH}-\text{CH}_2$

5 wherein n is 4 to about 20, and the acrylic anhydride polymer binder component (a).

18. The coating composition according to Claim 1 containing about 0.1-200% by weight, based on the weight of binder, of pigment.

10            19.     A substrate coated with a cured layer of the  
composition according to Claim 1.

20. The substrate according to Claim 19 wherein said substrate is plastic, metal, glass, silicon, concrete or wood.



## INTERNATIONAL SEARCH REPORT

Inter      nal Application No  
PCT/US 94/04963A. CLASSIFICATION OF SUBJECT MATTER  
IPC 5    C09D133/06    C09D127/12    C09D163/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5    C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,A	EP,A,0 572 254 (NIPPON PAINT) 1 December 1993 see page 2, line 24 - page 3, line 12 see page 3, line 19 - line 35 see page 4, line 19 - line 24 see page 5, line 16 - line 23 see page 9, line 15 - line 16; example 1 see claims 1-5 ---	1-4,9
A	EP,A,0 249 048 (AUSIMONT) 16 December 1987 see page 2, line 11 - line 15 see page 6, line 25 - line 35 see page 7, line 16 - line 19 see claims 1-5 -----	1,3

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance  
"E" earlier document but published on or after the international filing date  
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)  
"O" document referring to an oral disclosure, use, exhibition or other means  
"P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention  
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone  
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.  
"&" document member of the same patent family

Date of the actual completion of the international search

22 August 1994

Date of mailing of the international search report

05. 09. 94

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 94/04963

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0572254	01-12-93	JP-A- 6057077	01-03-94
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		JP-A- 63022823	30-01-88
		SU-A- 1660584	30-06-91
		US-A- 4816545	28-03-89
		ZA-A- 8703313	02-11-87
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DERWENT-ACC-NO: 1995-006741

DERWENT-WEEK: 200354

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**TITLE:** Anhydride epoxy coating compsn. modified with a fluoro-polymer useful for exterior finishing of automobiles and trucks, has improved durability, superior environmental resistance, excellent adhesion etc.

**INVENTOR:** ANDERSON A G; BARSOTTI R J

**PATENT-ASSIGNEE:** DU PONT DE NEMOURS & CO E I[DUPO]

**PRIORITY-DATA:** 1993US-061984 (May 14, 1993)

**PATENT-FAMILY:**

PUB-NO	PUB-DATE	LANGUAGE
WO 9426830 A1	November 24, 1994	EN
EP 702709 A1	March 27, 1996	EN
JP 08510287 W	October 29, 1996	JA
EP 702709 B1	January 28, 1998	EN
DE 69408317 E	March 5, 1998	DE
JP 3435653 B2	August 11, 2003	JA

**DESIGNATED-STATES:** CA JP AT BE CH DE DK ES FR GB GR IE IT LU MC  
NL PT SE DE FR GB IT NL DE FR GB IT NL

**APPLICATION-DATA:**



PUB-NO	APPL-DESCRIPTOR	APPL-NO	APPL-DATE
WO1994026830A1	N/A	1994WO-US04963	May 10, 1994
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JP 08510287W	N/A	1994WO-US04963	May 10, 1994
EP 702709B1	N/A	1994WO-US04963	May 10, 1994
DE 69408317E	N/A	1994WO-US04963	May 10, 1994
JP 3435653B2	Based on	1994WO-US04963	May 10, 1994

## INT-CL-CURRENT:

TYPE	IPC DATE
CIPP	C09D127/12 20060101
CIPS	C09D133/02 20060101
CIPS	C09D133/04 20060101
CIPS	C09D133/06 20060101
CIPS	C09D135/00 20060101
CIPS	C09D163/00 20060101

ABSTRACTED-PUB-NO: WO 9426830 A1



**BASIC-ABSTRACT:**

A coating compsn. comprising: 20-80 wt.% binder components (a) - (d); and 80-20% wt. organic liq. solvent; the binder comprising: (a) 25-90 wt.% acrylic anhydride polymer having at least 2 reactive anhydride gps., comprising units derived from (i) ethylenically unsatd. anhydride or ethylenically unsatd. dicarboxylic acid converted to an anhydride, and (ii) 1-12C alkyl (meth) acrylate(s), and having Mw 2,000 - 50,000; (b) 5-30 wt.% oxiranyl component having at least 2 reactive oxiranyl gps.; (c) 1-30 wt.% fluorinated polymer derived from monomer(s) having a perfluorocarbon gp. contg. at least 4 C and functional gp(s). that can react with (a) and/or (b); (d) an effective amt. of curing catalyst; and opt (e) 5-30 wt.% acrylic, polyester and/or polyester urethane resins opt. contg. hydroxyl and/or acid functionality. Also claimed is a substrate coated with a curved layer of the above compsn.

USE - The coating compsn. is esp. useful for exterior finishing of automobiles and trucks. as a coloured finish or partic. a clear coat.

ADVANTAGE - The fluoro-polymer gives the coating improved durability, providing a high quality finish with superior environmental resistance. It exhibits excellent substrate adhesion, good outdoor weatherability, etch and mar resistance and gloss.

**TITLE-TERMS: ANHYDRIDE EPOXY COATING COMPOSITION MODIFIED  
FLUORO POLYMER USEFUL EXTERIOR FINISH  
AUTOMOBILE TRUCK IMPROVE DURABLE SUPERIOR  
ENVIRONMENT RESISTANCE ADHESIVE**

**DERWENT-CLASS: A14 A26 A82 G02**

**CPI-CODES: A04-E10; A04-F01A1; A05-A01E4; A05-E01D; A05-G02; A08-C01; A08-D01; A12-B01B; A12-T05; G02-A02B1; G02-A02C; G02-A02E; G02-A02G; G02-A02H;**



**ENHANCED-POLYMER-INDEXING:** Polymer Index [1.1] 017 ; G0760\*R  
 G0022 D01 D51 D53 E00 D65 D31 D23  
 D22 D42 F39; G0760 G0022 D01 D23  
 D22 D31 D42 D51 D53 D59 D65 D84 F39  
 E00 E01 R00843 790; G0022\*R D01 D51  
 D53 D65 F39; G0102 G0022 D01 D02  
 D12 D10 D19 D18 D31 D51 D53 D58  
 D88 R00708 368; G0340\*R G0339  
 G0260 G0022 D01 D12 D10 D51 D53  
 D58 D63 F41 D11 D84 D85 D86 D87 D88  
 D89 D90 D91 D92 D93; G0384\*R G0339  
 G0260 G0022 D01 D12 D10 D51 D53  
 D58 D63 F41 D11 D85 D86 D87 D88 D89  
 D90 D91 D92 D93; H0022 H0011; H0033  
 H0011; L9999 L2391; L9999 L2073;  
 M9999 M2073; H0226; M9999 M2186;  
 L9999 L2391; L9999 L2186\*R; S9999  
 S1627 S1605; P1741; P0088;

Polymer Index [1.2] 017 ; G0351\*R  
 G0340 G0339 G0260 G0022 D01 D11  
 D10 D12 D51 D53 D58 D63 D87 F41;  
 G0102 G0022 D01 D02 D12 D10 D19  
 D18 D31 D51 D53 D58 D88 R00708 368;  
 G0760 G0022 D01 D12 D10 D51 D53  
 D58 D60 D85 F37 F35 E00 E03 R00654  
 7490; G0793 G0760 G0022 D01 D51  
 D53 D12 D10 D23 D22 D31 D42 D58  
 D65 D85 F39 E03 E00; H0033 H0011;  
 H0226; M9999 M2186; L9999 L2186\*R;  
 L9999 L2391; L9999 L2073; M9999  
 M2073; S9999 S1627 S1605; P1741;  
 P0088;

Polymer Index [1.3] 017 ; ND01; ND04;  
 K9676\*R; K9712 K9676; K9574 K9483;  
 K9552 K9483; K9529 K9483; K9585  
 K9483; K9610 K9483; K9609 K9483;  
 Q9999 Q7170 Q7158 Q7114; B9999  
 B5287 B5276; B9999 B4728 B4568;  
 B9999 B5301 B5298 B5276; B9999  
 B4411 B4400 B4240; B9999 B4397  
 B4240; B9999 B4262 B4240; Q9999  
 Q9234 Q9212; B9999 B5243\*R B4740;



N9999 N6780\*R N6655; N9999  
N6804\*R N6655; N9999 N7147 N7034  
N7023; Q9999 Q6791; Q9999 Q7114\*R;

Polymer Index [1.4] 017 ; H0226;

Polymer Index [1.5] 017 ; F51; A999  
A157\*R;

Polymer Index [1.6] 017 ; D01 D11 D10  
D23 D22 D45 D31 D53 D51 D59 D88  
F68; A999 A157\*R;

Polymer Index [1.7] 017 ; G2595\*R D01  
D11 D10 D50 D63 D86 F41; A999 A475;

Polymer Index [1.8] 017 ; A999 A102  
A077;

Polymer Index [2.1] 017 ; G1161 G1150  
G1149 G1092 D01 D11 D10 D19 D18  
D32 D50 D93 F32 F30 R00470 9523;  
G1570 G1558 D01 D11 D10 D23 D22  
D31 D42 D50 D69 D83 F47 CI 7A  
R00798 478; H0022 H0011; P0464\*R  
D01 D22 D42 F47; L9999 L2391; L9999  
L2073; M9999 M2073; S9999 S1627  
S1605; M9999 M2391; H0226; P0475;

Polymer Index [2.2] 017 ; G0340 G0339  
G0260 G0022 D01 D11 D10 D12 D23  
D22 D31 D42 D51 D53 D58 D63 D86 F47  
F41 R00799 129519; G0384 G0339  
G0260 G0022 D01 D11 D10 D12 D23  
D22 D31 D42 D51 D53 D58 D63 D87 F47  
F41 R00800 49004; H0011\*R; P0464\*R  
D01 D22 D42 F47; L9999 L2391; L9999  
L2073; M9999 M2073; S9999 S1627  
S1605; H0226; M9999 M2391; P0088;

Polymer Index [2.3] 017 ; P0500 F\* 7A;  
S9999 S1627 S1605; H0226; M9999  
M2391; L9999 L2391;



Polymer Index [2.4] 017 ; G0022 D01  
D12 D10 D51 D53 D59 D69 D82 F\* 7A  
R00975 104333; H0000; H0237\*R;  
M9999 M2324; M9999 M2186; M9999  
M2153\*R; S9999 S1627 S1605; H0226;  
M9999 M2391; L9999 L2391; P0511;

Polymer Index [2.5] 017 ; G1570\*R  
G1558 D01 D11 D10 D23 D22 D31 D42  
D50 D69 D83 F47 7A; G1070 G0997 D01  
D11 D10 D50 D86 F29 F26 R00032  
107456; H0011\*R; P0464\*R D01 D22  
D42 F47; S9999 S1627 S1605; H0226;  
M9999 M2391; L9999 L2391;

Polymer Index [2.6] 017 ; G0395\*R  
G0384 G0339 G0260 G0022 D01 D11  
D10 D12 D51 D53 D58 D63 D88 F41;  
G0384 G0339 G0260 G0022 D01 D11  
D10 D12 D23 D22 D31 D42 D51 D53  
D58 D63 D87 F47 F41 R00800 49004;  
H0022 H0011; P0464\*R D01 D22 D42  
F47; S9999 S1627 S1605; H0226; L9999  
L2391; M9999 M2391; P0088;

Polymer Index [2.7] 017 ; H0022 H0011;  
G1343\*R G1310 D01 D60 F37 F35 E00  
G1376\*R F38 E30; G1570\*R G1558 D01  
D11 D10 D23 D22 D31 D42 D50 D69  
D83 F47 7A; P0464\*R D01 D22 D42 F47;  
L9999 L2391; L9999 L2073; M9999  
M2073; S9999 S1627 S1605; H0226;  
M9999 M2391;

Polymer Index [2.8] 017 ; H0022 H0011;  
G1025\*R G0997 D01 F28 F26 G1070\*R  
F29; G1570\*R G1558 D01 D11 D10 D23  
D22 D31 D42 D50 D69 D83 F47 7A;  
P0464\*R D01 D22 D42 F47; L9999  
L2391; L9999 L2073; M9999 M2073;  
H0226; M9999 M2391;

Polymer Index [2.9] 017 ; H0022 H0011;



D23 D22 D42 D45 F19 F47 F34 G2324  
 D01; G1570\*R G1558 D01 D11 D10 D23  
 D22 D31 D42 D50 D69 D83 F47 7A;  
 P0464\*R D01 D22 D42 F47; L9999  
 L2391; L9999 L2073; M9999 M2073;  
 S9999 S1627 S1605; H0226; M9999  
 M2391;

Polymer Index [2.10] 017 ; G0022 D01  
 D12 D10 D51 D53 D59 D69 D82 F\* 7A  
 R00975 104333; H0000; H0237\*R;  
 M9999 M2175; M9999 M2153\*R; H0226;  
 M9999 M2186; L9999 L2153\*R; L9999  
 L2186\*R; S9999 S1627 S1605; M9999  
 M2391; L9999 L2153\*R; P0511;

Polymer Index [2.11] 017 ; ND01; ND04;  
 K9676\*R; K9712 K9676; K9574 K9483;  
 K9552 K9483; K9529 K9483; K9585  
 K9483; K9610 K9483; K9609 K9483;  
 Q9999 Q7170 Q7158 Q7114; B9999  
 B5287 B5276; B9999 B4728 B4568;  
 B9999 B5301 B5298 B5276; B9999  
 B4411 B4400 B4240; B9999 B4397  
 B4240; B9999 B4262 B4240; Q9999  
 Q9234 Q9212; B9999 B5243\*R B4740;  
 N9999 N6780\*R N6655; N9999  
 N6804\*R N6655; N9999 N7147 N7034  
 N7023; Q9999 Q6791; Q9999 Q7114\*R;

Polymer Index [2.12] 017 ; H0226;

Polymer Index [2.13] 017 ; A999 A102  
 A077;

Polymer Index [2.14] 017 ; G2595\*R  
 D01 D11 D10 D50 D63 D86 F41; A999  
 A475;

Polymer Index [2.15] 017 ; F51; A999  
 A157\*R;

Polymer Index [2.16] 017 ; D01 D11 D10



D23 D22 D45 D31 D53 D51 D59 D88  
F68; A999 A157\*R;

Polymer Index [3.1] 017 ; D60 F26\*R  
F35\*R; P0931\*R P1592 P0839 H0260  
H0011 H0044 F41 F77 D01 D63; L9999  
L2391; L9999 L2073; M9999 M2073;  
S9999 S1627 S1605;

Polymer Index [3.2] 017 ; B9999 B4900  
B4740; B9999 B4751 B4740; Q9999  
Q6791;

Polymer Index [3.3] 017 ; ND01; ND04;  
K9676\*R; K9712 K9676; K9574 K9483;  
K9552 K9483; K9529 K9483; K9585  
K9483; K9610 K9483; K9609 K9483;  
Q9999 Q7170 Q7158 Q7114; B9999  
B5287 B5276; B9999 B4728 B4568;  
B9999 B5301 B5298 B5276; B9999  
B4411 B4400 B4240; B9999 B4397  
B4240; B9999 B4262 B4240; Q9999  
Q9234 Q9212; B9999 B5243\*R B4740;  
N9999 N6780\*R N6655; N9999  
N6804\*R N6655; N9999 N7147 N7034  
N7023; Q9999 Q6791; Q9999 Q7114\*R;

Polymer Index [3.4] 017 ; A999 A102  
A077;

Polymer Index [3.5] 017 ; G2595\*R D01  
D11 D10 D50 D63 D86 F41; A999 A475;

Polymer Index [3.6] 017 ; F51; A999  
A157\*R;

Polymer Index [3.7] 017 ; D01 D11 D10  
D23 D22 D45 D31 D53 D51 D59 D88  
F68; A999 A157\*R;

Polymer Index [4.1] 017 ; P0000;

Polymer Index [4.2] 017 ; N9999 N7147



N7034 N7023; N9999 N7090 N7034  
 N7023; K9676\*R; K9574 K9483; B9999  
 B5447 B5414 B5403 B5276;

Polymer Index [5.1] 017 ; D60 F26\*R  
 F35\*R; P0088\*R; L9999 L2391; L9999  
 L2073; M9999 M2073; S9999 S1627  
 S1605;

Polymer Index [5.2] 017 ; D60 F26\*R  
 F35\*R; P0839\*R F41 D01 D63; L9999  
 L2391; L9999 L2073; M9999 M2073;  
 S9999 S1627 S1605;

Polymer Index [5.3] 017 ; G1025 G0997  
 D01 D11 D10 D50 D82 F28 F26 R00822  
 21; G1401 G1398 D01 D11 D10 D24 D22  
 D32 D42 D50 D65 D89 F39 E00 E25  
 R08834 131624; H0011\*R; P0839\*R F41  
 D01 D63; S9999 S1627 S1605; L9999  
 L2391; L9999 L2073; M9999 M2391;  
 M9999 M2073;

Polymer Index [5.4] 017 ; ND01; ND04;  
 K9676\*R; K9712 K9676; K9574 K9483;  
 K9552 K9483; K9529 K9483; K9585  
 K9483; K9610 K9483; K9609 K9483;  
 Q9999 Q7170 Q7158 Q7114; B9999  
 B5287 B5276; B9999 B4728 B4568;  
 B9999 B5301 B5298 B5276; B9999  
 B4411 B4400 B4240; B9999 B4397  
 B4240; B9999 B4262 B4240; Q9999  
 Q9234 Q9212; B9999 B5243\*R B4740;  
 N9999 N6780\*R N6655; N9999  
 N6804\*R N6655; N9999 N7147 N7034  
 N7023; Q9999 Q6791; Q9999 Q7114\*R;

Polymer Index [5.5] 017 ; F51; A999  
 A157\*R;

Polymer Index [5.6] 017 ; D01 D11 D10  
 D23 D22 D45 D31 D53 D51 D59 D88  
 F68; A999 A157\*R;



**Polymer Index [5.7] 017 ; A999 A102  
A077;**

**Polymer Index [5.8] 017 ; G2595\* R D01  
D11 D10 D50 D63 D86 F41; A999 A475;**

**SECONDARY-ACC-NO:**

**CPI Secondary Accession Numbers: 1995-002394**